

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Improvements in or relating to Stable Ketene Dimer-Emulsifier Mixtures and their preparation

We, HERCULES POWDER COMPANY, a Corporation organized under the laws of the State of Delaware, one of the United States of America, of 900, Market Street, City of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel compositions containing a ketene dimer and an emulsifier therefor and to a process for making same.

It is possible to make aqueous emulsions of higher alkyl ketene dimers as disclosed in U.S. 2,627,477, issued to W. F. Downey. In making these emulsions, various types of emulsifiers may be used, including both the ionic and non-ionic types. The present invention is particularly concerned with the nonionic type emulsifiers for this purpose. In merchandising alkyl ketene dimers for industrial use it is desirable to ship the ketene dimers and the emulsifier as a mixture which the customer can easily convert to an emulsion as needed in his plant. Attempts to put this into practice have been unsuccessful heretofore due to the fact that variable results are oftentimes achieved as respects the emulsifiability of the composition and the quality of the emulsion formed. In general, the longer the mixtures of nonionic emulsifier and the ketene dimers are permitted to stand prior to use, the poorer and poorer become the emulsions produced therefrom, until finally emulsifiability is lost entirely.

It has now been found that there is a certain limited class of nonionic type emulsifiers that are unique in that they completely overcome the deficiency referred to above. Thus, these emulsifiers may be mixed with ketene dimers to form dimer-emulsifier mixtures which are stable over extended periods of time. This makes it possible to manufacture and distribute the dimer and emulsifier in the form

of a mixture which can easily and quickly be emulsified merely by the addition of water with accompanying agitation.

In general, the emulsifiers herein disclosed may be prepared by first reacting ethylene oxide with a hexitol, such as sorbitol, to form a polyoxyethylene ether of the hexitol. The polyoxyethylene ether of the hexitol may then be reacted with a 12 to 20 carbon atom fatty acid to form an ester which is then treated to reduce the hydroxyl number as required. The emulsifier may then be mixed with the ketene dimer to form the stable dimer-emulsifier mixture hereinabove referred to.

Having described the invention generally, the following examples are given to illustrate specific embodiments thereof. In the examples, parts are by weight unless otherwise specified.

#### EXAMPLE 1.

This example illustrates the preparation of an acetylated polyoxyethylene sorbitol oleate and its effectiveness in forming a stable mixture with an alkyl ketene dimer. In the preparation 0.625 mole of oleic acid was employed for each hydroxyl equivalent of the polyoxyethylene ether. Fourteen hundred and ten parts of oleic acid and 2382 parts of the mixed polyoxyethylene ether, prepared by reacting 182 parts of an aqueous solution of sorbitol containing 85% sorbitol with 2200 parts of ethylene oxide, were charged into an agitated reaction vessel, together with a catalyst consisting of 6.64 parts sodium hydroxide.

The charge was reacted in an atmosphere of carbon dioxide at a temperature of 245° C. to an acid number less than 5. This required from 3 to 4 hours. The resulting product, which had a saponification number of about 75 and a hydroxyl number of about 60, was cooled to 90° C. and phosphoric acid added in an amount equivalent to the amount of catalyst employed.

A portion of the product, prepared as des-

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polyoxyethylene ether. The procedure of Example 1 was followed in reacting together 883 parts double pressed stearic acid, 1367 parts of the mixed polyoxyethylene ether, prepared by reacting 182 parts of an aqueous solution of sorbitol (85% sorbitol) with 2200 parts of ethylene oxide, and 3.93 parts sodium hydroxide (as catalyst). The resulting product had an acid number of 2.4, a saponification number of 84, and a hydroxyl number of 55. The material was acetylated utilizing the procedure of Example 1. The acetylated product had an acid number of 1.6, a saponification number of 130, and a hydroxyl number of 2. Mixtures of the acetylated material with the ketene dimers described in Example 1 in a ratio of about 1:5 were stable over relatively long periods of time as evidenced by their ability to form good emulsions after storage in a 45° C. oven for 13 days. By comparison, emulsions produced from mixtures of the unacetylated material with ketene dimers rapidly depreciated in quality even when stored at room temperatures and after standing for 7 days were of poor quality.

#### EXAMPLE 6.

This example illustrates the preparation of an acetylated polyoxyethylene sorbitol ester from a mixture of fatty acids and its effectiveness in forming a stable mixture with an alkyl ketene dimer. The procedure of Example 5 was repeated employing in place of the 883 parts double pressed stearic acid, 503 parts of a hydrogenated tallow fatty acid containing about 70% stearic acid and about 30% palmitic acid, 345 parts of a commercial grade palmitic acid containing 90% palmitic acid, 6% stearic acid, and 4% oleic acid and sold under the trade name "Neo Fat 16" by Armour & Company, and 35 parts of a high grade distilled oleic acid sold under the trade name "Emery 233LL". The dimer-emulsifier mixtures were stable over an extended period of time as evidenced by their ability to form good emulsion after storage in a 45° C. oven for 13 days. By comparison, emulsions produced from mixtures of the unacetylated material with ketene dimers rapidly depreciated in quality even when stored at room temperatures so that at the end of 7 days they were of poor quality.

#### EXAMPLE 7.

This example illustrates the preparation of an acetylated polyoxyethylene sorbitol ester from refined tall oil fatty acids and its effectiveness in forming a stable mixture with an alkyl ketene dimer. In the preparation, 0.5 acid equivalent of the refined tall oil fatty acids was employed for each hydroxyl equivalent of the polyoxyethylene ether. Thirteen hundred twelve parts of refined tall oil containing 47—51% fatty acids, 42—46% resin acids, a maximum of 7.8% unsaponifiables, and 0.1% moisture, 1942 parts of the mixed polyoxy-

ethylene ether, prepared by reacting 182 parts of an aqueous solution of sorbitol (85% sorbitol) with 1760 parts of ethylene oxide, and 5.7 parts sodium hydroxide (as catalyst) were reacted at 265—275° C. in an atmosphere of carbon dioxide to an acid number less than 20. The product was cooled to 90° C. and 2.56 cc. of phosphoric acid added. The resulting material had an acid number of 18, a saponification number of 56 and a hydroxyl number of 98. After acetylation (utilizing the procedure of Example 1) the material had an acid number of 14, a saponification number of 132 and a hydroxyl number of 5. Satisfactory emulsions were obtained from mixtures of the acetylated material with ketene dimers of the type set forth in Example 1 after storage in a 45° C. oven for 13 days. On the other hand, emulsions produced from mixtures of the unacetylated material with ketene dimers rapidly depreciated in quality and at the end of 7 days were of very poor quality.

#### EXAMPLE 8.

This example illustrates the preparation of an acetylated polyoxyethylene sorbitol ester from refined tall oil fatty acids and its effectiveness in forming a stable mixture with an alkyl ketene dimer. In the preparation, 0.75 acid equivalent of the tall oil fatty acids was employed for each hydroxyl equivalent of the polyoxyethylene ether. Two hundred seventy-six parts of refined tall oil as defined in Example 7, 324 parts of the mixed polyoxyethylene ether, prepared by reacting 182 parts of an aqueous solution of sorbitol (85% sorbitol) with 2200 parts ethylene oxide, and 0.97 parts sodium hydroxide (D.B.) were reacted at 255° C. in an atmosphere of carbon dioxide to an acid number of 26—28. The product was cooled to 90° C. and 0.437 cc. of phosphoric acid (85%) added. The resulting material had an acid number of about 27.5, a saponification number of about 65, and a hydroxyl number of about 65, and a hydroxyl number of 72. After acetylation (utilizing the procedure of Example 1) the material had an acid number of 23.8, a saponification number of 118 and a hydroxyl number of 4. Satisfactory emulsions were obtained from mixtures of the acetylated material with ketene dimers of the type set forth in Example 1 after storage in a 45° C. oven for 13 days. By comparison, emulsions produced from mixtures of the unacetylated material with ketene dimers rapidly depreciated in quality and after standing for 7 days were of poor quality.

#### EXAMPLE 9.

A mixture of 98 parts of alkyl ketene dimer prepared from a mixture of fatty acids containing 45% stearic acid and 55% palmitic acid and 2 parts of a mixture of fatty acids containing 45% stearic acid and 55% palmitic acid was mixed in one case with 20 parts of the



control, are obtained. This will usually take from 2 to 8 hours. The product is then cooled to about 90° C. and an acid, for example, phosphoric acid, added to neutralize the alkali.

5 If color is an important consideration, the reaction can be carried out in the presence of activated carbon. The activated carbon may be filtered out at the completion of the above reaction or alternatively may be carried through the subsequent treatment for reducing the hydroxyl number.

10 The reduction of the hydroxyl number may be accomplished by any suitable mechanism which will mask or otherwise cover up the reactive hydroxyl groups without changing, or substantially changing, the emulsifying properties of the material. The preferred mechanism for accomplishing this is acylation with, for example, the anhydrides or acid chlorides of lower fatty acids such as acetic acid and propionic acid. Ketenes, such as ketene, and methyl ketene, may also be used. Alternatively, the material may be esterified by reacting with isocyanate to form carbamate ester.

25 Alkylation is also effective in accomplishing the desired reduction of the hydroxyl number. Thus, for example, the hydroxyl containing material may be subjected to an etherification reaction utilizing (1) dimethyl sulfate in the presence of an alkali or (2) an alkyl iodide in the presence of a sodium derivative of the hydroxyl containing material. Alternatively, the hydroxy component of the material may be condensed with an olefin, such as isobutylene, in the presence of an acid catalyst, such as sulfuric acid, to form isobutyl ether. Cyano-ethylation may also be used by reacting the hydroxy component of the material with acrylonitrile in the presence of a tertiary amine.

40 While it is apparent from the above that various types of reactions may be utilized to cover or mask the hydroxyls of the material, the most preferred procedure is acetylation with acetic anhydride wherein an excess of acetic anhydride, usually about 10% excess, is employed. The hydroxyl number of the emulsifier to be acylated is utilized in calculating the amount of acetic anhydride required.

50 If it is desired to improve the color of the product, it is bleached with a bleaching agent at 100° C. The product is subjected to vacuum after bleaching to reduce the water content below 0.5%. The amount of the bleaching agent used is usually 0.5 to 1% based on the charge.

55 The relative proportions of the ketene dimer and emulsifying agent may be varied as desired, depending principally on the ultimate use contemplated for the composition. In general, however, the emulsifier will comprise from 5% to 30% or more by weight of the composition and preferably from 13% to 17%. Actually, the upper limit is set because of economic reasons, and not because of

inoperability, when larger amounts of emulsifier are used.

The compositions of the invention are easily and quickly emulsified by the addition of warm water. For use in the treatment of cellulosic materials such as, for example, paper and the like, the composition will generally be employed in dilute form usually containing between 0.01 and 2.0% and preferably between 0.1 and 0.6% of the ketene dimer.

What we claim is:—

1. A composition comprising a ketene dimer and an emulsifier therefor, said emulsifier comprising an ester of a 12 to 20 carbon atom fatty acid with a polyoxyethylene ether of a hexitol containing from 30 to 75 oxyethylene groups per mole, the ratio of fatty acid to polyoxyethylene ether of hexitol being from 0.5 to 0.85 mole of fatty acid per hydroxyl equivalent of the ether, the hydroxyl number of said emulsifier having been reduced to less than 10.

2. A composition as set forth in Claim 1 in which the emulsifier is an acylation product.

3. A composition as set forth in Claim 2 in which said acylation product is an acetylation product.

4. A composition as set forth in Claim 1 in which the emulsifier is an alkylation product of said ester.

5. A composition as set forth in Claim 1 in which the emulsifier is an etherification product of said ester.

6. A composition as set forth in any of Claims 1—3 in which the emulsifier comprises the acetylation product of the mixed ester obtained by reacting a 12 to 20 carbon atom fatty acid with a polyoxyethylene ether obtained by condensing ethylene oxide with a hexitol in a ratio of from 1320 parts by weight to 3300 parts by weight of ethylene oxide to 182 parts by weight of the hexitol.

7. A composition as set forth in any of the preceding claims in which the hexitol is sorbitol.

8. A composition as set forth in any of the preceding claims in which the fatty acid is oleic acid, stearic acid or a mixture of fatty acids such as tall oil.

9. The method of forming a stable emulsifiable mixture of ketene dimer and nonionic emulsifier which comprises reacting ethylene oxide with a hexitol in a mole ratio of from 30 to 75 moles of ethylene oxide per mole of the hexitol to form a polyoxyethylene ether of the hexitol, reacting the polyoxyethylene ether of the hexitol with a 12 to 20 carbon atom fatty acid in a ratio from 0.5 to 0.85 mole of fatty acid per hydroxyl equivalent of the polyoxyethylene ether to form an ester, treating the ester with either an acylating, alkylating or etherifying agent, to reduce the hydroxyl number below about 10 and adding the resulting material to a ketene dimer.

10. The method set forth in Claim 9 in which the hexitol is sorbitol.